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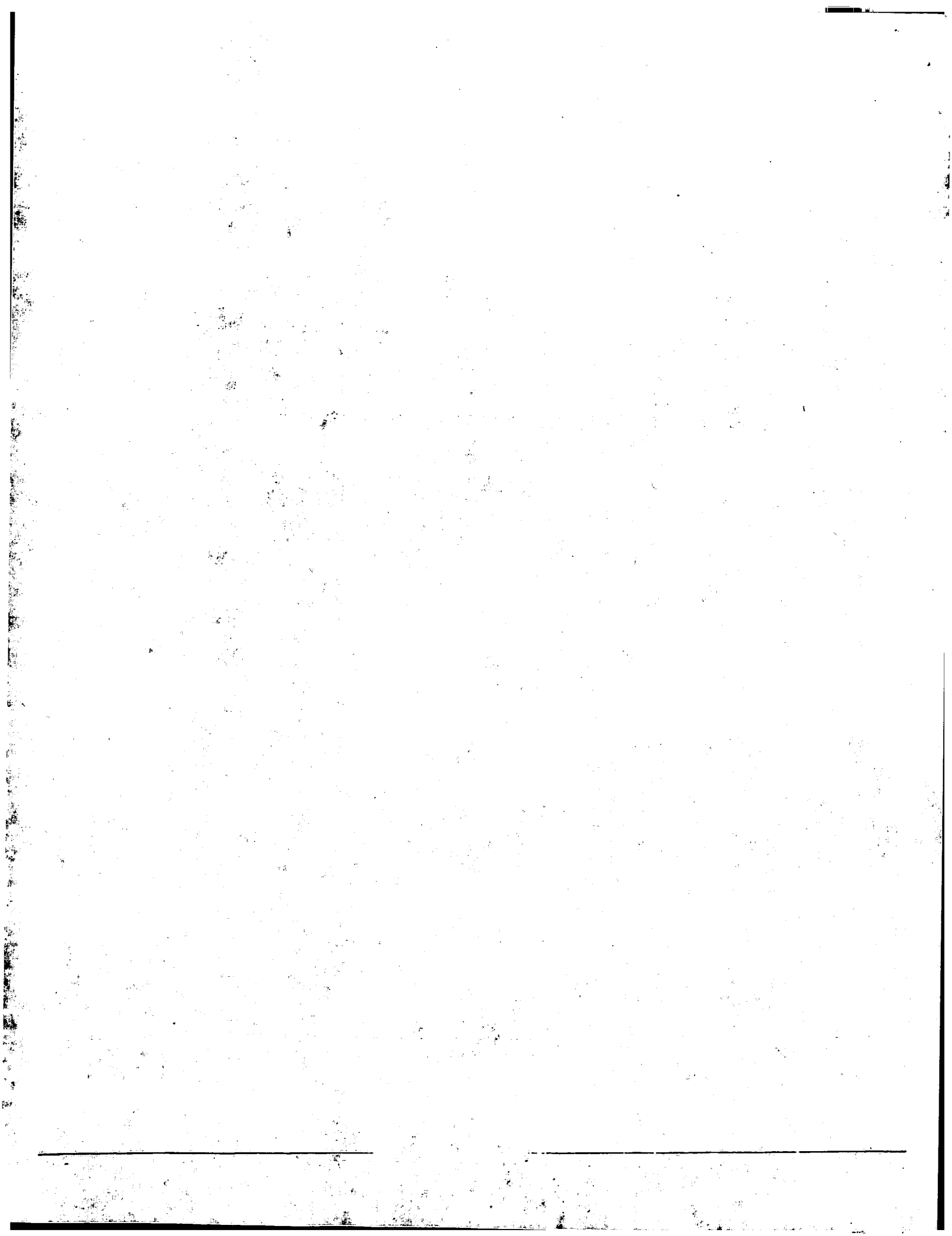
**Interactions of PEO-containing polymeric surfactants with
hydrophobic surfaces**

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The University of Utah, 1988

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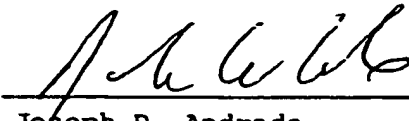


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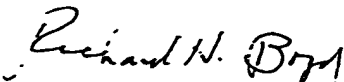
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ABSTRACT

There are many applications where materials and devices must contact various aqueous media, including biologic and physiologic solutions. Such media often contain proteins which can adsorb and/or aggregate at interfaces. Surfaces which nonspecifically repel all proteins are desirable and often necessary to minimize the deposition and aggregation of proteins. Such surfaces are prepared by immobilizing neutral, hydrophilic polymers. Among hydrophilic polymers, a particularly effective polymer for protein-resistant surfaces appears to be polyethylene oxide (PEO).

Two types of nonionic polymeric surfactants, PEO-containing block copolymer surfactants (commercial) and PEO-grafted polymeric surfactants (synthesized), were studied as a possible means to produce PEO-rich surfaces as protein-resistant surfaces by a simple coating treatment of common hydrophobic medical materials. The PEO-containing polymeric surfactants were also studied as a possible means to remove proteins pre-adsorbed on the hydrophobic surfaces.

Efficient removal of adsorbed proteins is needed for many surfaces which have direct contact with biological systems.

Surface properties of the surfactants (surface tension at air/water interfaces, adsorption properties of the

surfactants on hydrophobic surfaces (dimethyldichloro silane (DDS)-coated glass, low density polyethylene (LDPE), and polyalkyl methacrylates (PAMA) surfaces), protein (human albumin and plasma)-resistant character of the prepared PEO surfaces, and effectiveness of the surfactants for removal of proteins pre-adsorbed on the surfaces) were investigated by the Wilhelmy plate surface tension technique, by X-ray photoelectron spectroscopy (XPS), and by using ^{125}I -labeled surfactants and ^{125}I -labeled proteins. The surface properties of the commercially available PEO-containing block copolymer surfactants were compared with those of the synthesized PEO-grafted polymeric surfactants.

The data presented in this study indicate that PEO-grafted polymeric surfactants with a high portion of hydrophobic segments (up to 90 mol %) and long PEO chains (mol.wt. 1,900 or 4,000) have effective protein-resistant properties (the surfaces treated with those surfactants decreased the adsorption of human albumin and plasma more than 90 % compared to untreated surfaces), while the PEO-containing block copolymer surfactants show effective removal properties of the pre-adsorbed proteins (more than 90 % removal of the proteins from surfaces).

The possible mechanisms for the protein resistance and removal of pre-adsorbed proteins by the PEO-containing polymeric surfactants were discussed in this study.

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CHAPTER 2

SOLUTION PROPERTIES OF POLYETHYLENE OXIDE IN WATER

2.1 General Features

Polyethylene oxide (PEO) is a crystalline, thermoplastic polymer. It is an uncharged polyether with the chemical formula, $\text{H}-(\text{OCH}_2\text{CH}_2)_n-\text{OH}$, which is the simplest structure of water-soluble polymers. Unlike most polymer systems, PEO is commercially available in an extraordinarily wide range of molecular weights from 200 to several million or more. The lower molecular weight members of the series, with chain lengths up to about 150, are known as polyethylene glycols. The higher members of the series are known as polyethylene oxides or as polyoxyethylenes. The properties of these classes of compounds differ greatly because of the large differences in molecular weight, as seen in Table 2.1 (compiled from Ref.1).

By X-ray analysis [2], it is known that the PEO molecule in the crystalline state has a helical conformation which contains two turns in a fiber identity period (unit length of c-axis) of 19.3 Å. The crystallographic unit cell contains four molecular chains and is monoclinic with $a = 8.16 \text{ Å}$, $b = 12.99 \text{ Å}$, $c = 19.3 \text{ Å}$, and $\beta = 126^\circ 5'$. Table 2.2

Table 2.1
Properties of polyethylene oxides with different molecular weight^a

Properties	Number average molecular weight						
	200	400	600	1,000	4,000	6,000	20,000
Specific gravity (20/20 °C)	1.125	1.130	1.130	--	1.204	--	--
Melting point (°C)	--	4-8	20-25	37-40	53-56	60-63	50-55
Viscosity (cks., 210 °F)	4.3	7.3	10.5	17.4	75-85	700-900	--
Heat of fusion (cal/gm)	--	36	35	37	43	46	41
Refractive index (_D , 25 °C)	1.460	1.467	1.469	--	--	--	--
Surface tension (dynes/cm)	44.5	44.5	44.5	--	--	--	--

^aCompiled from Ref.1.

Table 2.2

Structures and properties of polyethers with a general formula, $\text{HO}\{-(\text{CH}_2)_m-\text{O}-\}_n\text{H}^a$

m	1	2	3	4	∞
Polymer	Polymethylene oxide	Polyethylene oxide	Polytri-methylene oxide	Polytetra-methylene oxide	Polymethylene (polyethylene)
Structural formula	$(-\text{CH}_2\text{O}-)_n$	$(-\text{CH}_2\text{CH}_2\text{O}-)_n$	$(-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_n$	$(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_n$	$(-\text{CH}_2-)_n$
Melting point ($^{\circ}\text{C}$)	180	60	34	36	137
Density (gr/cm^3)	1.40-1.51	1.15-1.26	--	1.08-1.18	0.92-1.00
Hardness	Hard	Soft	Soft	Soft	Medium
Molecular structure	9_5 helix	7_2 helix	Planar zigzag	Planar zigzag	Planar zigzag
Crystal structure ^b	Trigonal $a = 4.46 \text{ \AA}$ $c = 17.3 \text{ \AA}$	Monoclinic $a = 8.16 \text{ \AA}$ $b = 12.99 \text{ \AA}$ $c = 19.3 \text{ \AA}$ $\beta = 126^{\circ} 5'$	--	Monoclinic $a = 5.48 \text{ \AA}$ $b = 8.73 \text{ \AA}$ $c = 12.1 \text{ \AA}$ $\beta = 134^{\circ} 12'$	Orthorhombic $a = 7.40 \text{ \AA}$ $b = 4.93 \text{ \AA}$ $c = 2.534 \text{ \AA}$
	$N = 1$	$N = 4$		$N = 2$	$N = 2$

^aFrom Ref.2^b c , fiber axis; N , number of the molecular chains contained in a unit cell.

summarizes the structures and properties of a series of polyethers with a general formula, $\text{HO}[-(\text{CH}_2)_m\text{O}]_n\text{H}$. A more detailed structure analysis is, however, not possible by X-ray methods alone. The information concerning the conformation of the PEO chain in the crystalline and molten states as well as in solution has been obtained through analyses of the infrared [3-5], Raman [6-9], and NMR spectra [3,10-16]. In the crystalline state, infrared and Raman spectra analyses agree with the conformational assignment to internal rotation about the O-CH₂, CH₂-CH₂, and CH₂-O bonds of trans, gauche, trans, respectively. In the molten state, the conformation becomes somewhat disordered [4-6]. This disordering is noted principally by the appearance of a considerable fraction of trans, trans, trans conformations. In water solution, PEO chain retains to a large degree the trans, gauche, trans sequence and helical conformation of the crystalline state, as evidenced from IR spectra [4], Raman spectra [6], NMR spectra [3,4], and calorimetry [17].

In comparison with all other water-soluble resins (i.e., high molecular weight polymers), PEO resins are unique in a linearity of structure, nonionic character, and water solubility. This polymer displays a high degree of polymer-solvent interaction in water, which is observed in the development of structural viscosity to an unusual degree [18-22].

PEO has many interesting properties; however, our main

concern in this Chapter is its unique solution behavior in water.

2.2 Solubility and Molecular Structure of PEO in Water

At room temperature, PEO is completely miscible with water in all proportions for all degrees of polymerization [1]. The water solubility of PEO is unlimited, at least up to temperatures slightly below 100 °C. In contrast to the complete water solubility of PEO, closely related polymers such as polymethylene oxide, polytrimethylene oxide, polyacetaldehyde, and polypropylene oxide are water insoluble under ordinary conditions (Table 2.3, from Refs.1,19,23).

Why is PEO miscible in all proportions with water at room temperature, while other polyethers are not? It seems to be related to hydration of the ether oxygens in a manner which is apparently unique to the PEO structure [19,24,25]. Water is a highly structured liquid, with hydrogen bonds linking the individual molecules to each other. The precise arrangement about each molecule is not known, but the tetrahedral symmetry of the oxygen bond orbitals and the tetrahedral structure of ice suggest a locally tetrahedral arrangement of molecules in the liquid state also [26]. The highly connected network of tetrahedrally coordinated water molecules contains quite a large fraction of interstitial space, as established by X-ray and neutron diffraction [27].

Table 2.3
Structures and solubility of polyethers^a

Polymer	Structural unit	Solubility in water at room temperature
Polymethylene oxide	-CH ₂ -O-	No
Polyethylene oxide	-CH ₂ -CH ₂ -O-	Yes
Polytrimethylene oxide	-CH ₂ -CH ₂ -CH ₂ -O-	No
Polyacetaldehyde	-CH-O- CH ₃	No
Polypropylene oxide	-CH ₂ -CH-O- CH ₃	Partially ^b

^aFrom Refs.1,19,23

^bOnly oligomers (mol.wt ≤ 1,500) soluble.

This network is characterized by oxygen-oxygen distances of 2.85 Å between neighbors and 4.7 Å between next-nearest neighbors. Any arrangement of this type would have to be disrupted by any solute dissolved in water. Some hydrogen bonds would have to be broken; if the solute is polar, new hydrogen bonds between water and solute would be formed [26]. Kjellander and Florin [28,29] have intensively studied the PEO-water system and suggested that the water solubility of PEO can be explained in terms of a good structural fit between the water and the polymer. They suggested that PEO, in contrast to the other polyethers, can be fitted into this type of water lattice so that all of the lattice points are occupied, either by a water or by an ether oxygen, i.e., the conformation of the polymer can be arranged so that both the distances of neighboring and next-neighboring oxygen atoms fulfill the requirements of the water lattice (refer to Refs.28,29 for more discussion). The ethylene segments thus fill out voids in the spacious water structure without distortion of water lattice and minimally perturb the structure of water itself (see Section 2.6.1).

2.3 Solubility with Temperature

PEO exhibits an inverse solubility-temperature relationship [1,18,19,23,30]. One way of interpreting the inverse solubility-temperature relationship of PEO would be through a disordering of "hydration shells" that exist about

the polymer molecule at low temperatures [28,29,31-33]. These "hydration shells" correspond to a layer of highly oriented water which would surround the polymer in aqueous solution. The coupling between the polymer and water gives rise to enhanced structuring of the water that is close to the polymer chain and this makes it necessary to distinguish between water in the hydration shell of PEO and in the bulk solution. The hydration shell water is characterized by both lower entropy and enthalpy than the bulk water [28]. Such a structure formation is entropically unfavorable, but this contribution to the free energy is overcome by the decrease in enthalpy, on the increased structuring of the water and the binding to PEO [28,29]. Thus, PEO is water soluble. The good fit between PEO and the water structure probably makes the enthalpy contribution significantly large. When the temperature is raised, the hydration shell is gradually broken down due to thermal motion. This means that the difference in properties between bulk and shell water decreases. Since the structure does not break down sufficiently rapidly when the temperature is raised, the unfavorable entropy contribution dominates and the system phase-separates, decreasing the extent of the enhanced structure (refer to Refs.28,29 for the detailed discussion). The phase separation or precipitation temperature depends on the polymer concentration [1]. For very dilute solutions (0.2 % or less polymer), the precipitation is observed as a

cloud point. For slightly more concentrated solutions (0.5 % or more polymer), the polymer precipitates as a gel. At even higher temperatures, when the structure has largely been broken down, the unfavorable entropy contribution is diminished [28,29]. The system is then completely miscible again, provided the temperature is not high enough to cause destruction of the polymer.

Doolittle [34] tried to interpret the inverse solubility-temperature relationships of high polymer-solvent systems. Solvophilic and solvophobic influences are considered to be reflected in the heat and entropy of dilution factors of the polymer-solvent interaction parameters. Thus the temperature dependence of the solubility is such that the solvent becomes a nonsolvent at a critical temperature. In PEO, the hydrophobic and hydrophilic character is provided by the alternate ethylene units (hydrophobic) and oxygens (hydrophilic) of the polymer chain. If the inverse solubility-temperature phenomenon is to be interpreted as a hydrophilic-hydrophobic balance in the polymer system, increasing the hydrophobic character of the polymer should result in a lowering of the polymer precipitation temperature. Bailey and Callard [19] used copolymers of ethylene oxide and propylene oxide to test this prediction. They showed that the precipitation temperature, at a given polymer concentration, decreases linearly with increasing propylene oxide content.

2.4 Mobility

The dynamic properties of a polymer depend on the probable polymer conformations and the transition probabilities. The presence of bulky groups attached to the backbone will introduce steric hindrances and reduce the mobility of polymer segments. The dynamic behavior of PEO in water was characterized by nuclear magnetic relaxation [35-38], electron spin resonance [38], and measurement of dynamic moduli [39]. PEO, an uncharged polymer without bulky groups, appeared to be very flexible, as compared with polymers with bulky groups (steric hindrances) or polyelectrolytes such as polymethacrylic acid (steric and electrostatic hindrances).

The dielectric behavior of PEO has been studied to elucidate polymer chain flexibility and polar bond interactions [1,40]. Davies et al. [41] found from dipole relaxation studies that there is a marked freedom of reorientation in PEO. They suggested that the carbon-oxygen linkage acts as a ball-and-socket joint, making the average freely moving unit little more than a single monomeric unit.

Breen et al. [35] studied the molecular weight dependence of the relaxation rates of PEO from NMR. They applied a dilute aqueous solution of PEO to avoid polymer-polymer interactions. They suggested that the molecular weight dependence is caused by end group contributions and in addition by overall tumbling (small molecules). They also suggested that the position dependence of the

relaxation rates along the chain disappears after some distance from the end and then the relaxation rate becomes the polymer relaxation rate. For long polymer chains, the contribution of end group dynamics in the relaxation rate will be insignificant. They did not observe any end group effect in ^1H -relaxation rates as the PEO chain length was greater than 100. It was also reported that the segmental motions of PEO are independent of chain length when the chain length is greater than about 100 [42] or about 130 [43-45].

Nagaoka et al. [37] also studied different PEO chains (attached on a surface) in a hydrated state according to NMR spectroscopy. They related the line width of the peak ^{13}C -NMR signal to the PEO chains. They found that increasing PEO chain length to 100 decreases the width of the signal peak, indicating increased mobility.

2.5 Heat and Entropy of Dilution

The heat and entropy of dilution of PEO in water were studied from the temperature dependence of the intrinsic viscosity [19,46], vapor pressure and heat of mixing experiments [47], and calorimetry [17,48-52]. It was calculated that both the heat of dilution and the entropy of dilution of PEO in water are negative. Negative values for these parameters implied a high degree of polymer-solvent interaction and orientation of solvent with respect to the polymer chain [46].

Maron and Filisko [17,52] used a microcalorimeter to measure the heats of dilution and solution of PEO in water and organic solvents. They found from the organic solvent data that the heat of fusion or "lattice energy" of the sample is independent of the solution concentration or the solvent used. However, there was a difference in the behavior of PEO in water compared to the organic solvents which was attributed to the difference in the conformation of the polymer in organic solvents and in water. PEO in organic solvents exists as a random coil, whereas in water its conformation is helical. They showed that the interconversion of the random coil to the helix involves a heat evolution (39.3 cal of heat per gram of polymer) and suggested that this heat evolution (or helix formation) probably accounts for the fact that PEO is water soluble in contrast to polymethylene oxide and polypropylene oxide.

Lakhanpal et al. [49-51] also measured the heats of solution of PEO in organic solvents and water and obtained results similar to those of Maron and Filisko; the values were independent of the nature of the solvent used beside water. The anomalous behavior of PEO in water is explained by the authors as a result of strong interaction via hydrogen bonds of water molecules with the ether oxygens of the polymer chains.

2.6 Comparison with Some Other Polymers

2.6.1 Comparison of Solubility with Other Polyethers

As suggested in Section 2.2, the difference between PEO and the water-insoluble polyethers (see Table 2.3) may be that the latter do not satisfy the structural fit to allow a mainly unstrained coupling to a continuously tetrahedrally coordinated network of water (oxygen-oxygen distances of 2.85 Å between neighbors and 4.7 Å between next-nearest neighbors of the lattice) around the polymer chains; PEO can be nicely fitted into this type of water lattice without distortion of the lattice so that all of the lattice points are occupied, either by a water or by an ether oxygen, i.e., the conformation of PEO can be arranged so that both the distances of neighboring and next-neighboring oxygen atoms fulfill the requirements of the water lattice and the ethylene segments fill out voids in the spacious water structure [29].

Consider polypropylene oxide (PPO). When PPO is introduced into water, it develops a hydration shell with an enhanced structuring of water as evidenced by the negative entropy and enthalpy of mixing [29,49,50]. Despite the fact that PPO has the same backbone structure as PEO, an optimal water structure cannot be formed, since the methyl groups of PPO constitute a steric hindrance. The strain of the water structure leads to a smaller hydrogen bond energy than in the case of PEO. That is the reason why PPO is partially

soluble in water for only oligomers. The smaller hydrogen bond energy due to the strain of water lattice also leads to the low precipitation temperature [29,53]. This suggestion is in accord with the fact that some copolymers of PEO and PPO are water soluble but have a lower precipitation temperature than PEO [54]. As the proportion of PPO increases, this temperature decreases [19]. When the methyl groups along the chain become more numerous, it would be expected that the strain in the water structure would increase, which makes the heat of mixing less negative and lowers the precipitation temperature.

In the case of polymethylene oxide (PMO), the distance between neighboring oxygens in PMO seems too short to be accommodated in a water structure [29]. It is in fact rather striking that PMO is not water soluble, although it has a larger oxygen/carbon ratio than PEO and does not have any side groups to cause steric hindrance. The distance between neighboring oxygens in the polyether as well as steric hindrance may be an important factor for the solubility of polyethers in water.

Polyacetaldehyde has practically the same oxygen-oxygen distance as PMO (see Table 2.3 for the structure). In an amorphous form it is freely soluble in many organic solvents but insoluble in water [54,55], because it also has too short a distance between neighboring oxygens to be accommodated in the water structure and has a side group to

cause steric hindrance.

2.6.2 Comparison of Thermodynamic Parameters with Other Water-Soluble Polymers

Common synthetic polymers that are soluble in water at normal temperatures are as follows (Figure 2.1):

Polyethylene oxide (PEO), polyacrylic acid (PAA), polyacrylamide (PAAm), polymethacrylic acid (PMAA), polymethacrylamide (PMAAm), polyvinyl alcohol (PVA), and polyvinylpyrrolidone (PVP).

Table 2.4 summarizes some thermodynamic parameters involved in the polymer-water interactions. From the Table, χ is called the "polymer-solvent" or "Flory-Huggins" interaction parameter, which is a measure of the interaction between a given solvent and a given polymer. It is a free energy parameter and a temperature-dependent quantity. By the Flory-Huggins theory [24,56], the free energy change of mixing of liquid and polymer to form the solution (ΔG_M) is defined as follows, by assuming that the polymer is completely amorphous and sufficiently large and that ΔG_M is originated in the replacement of some of the contacts between like species in the pure liquids with contacts between unlike species in the solution:

$$\Delta G_M = \Delta H_M - T\Delta S_M$$

$$\Delta H_M = RT\chi n_1 v_2$$

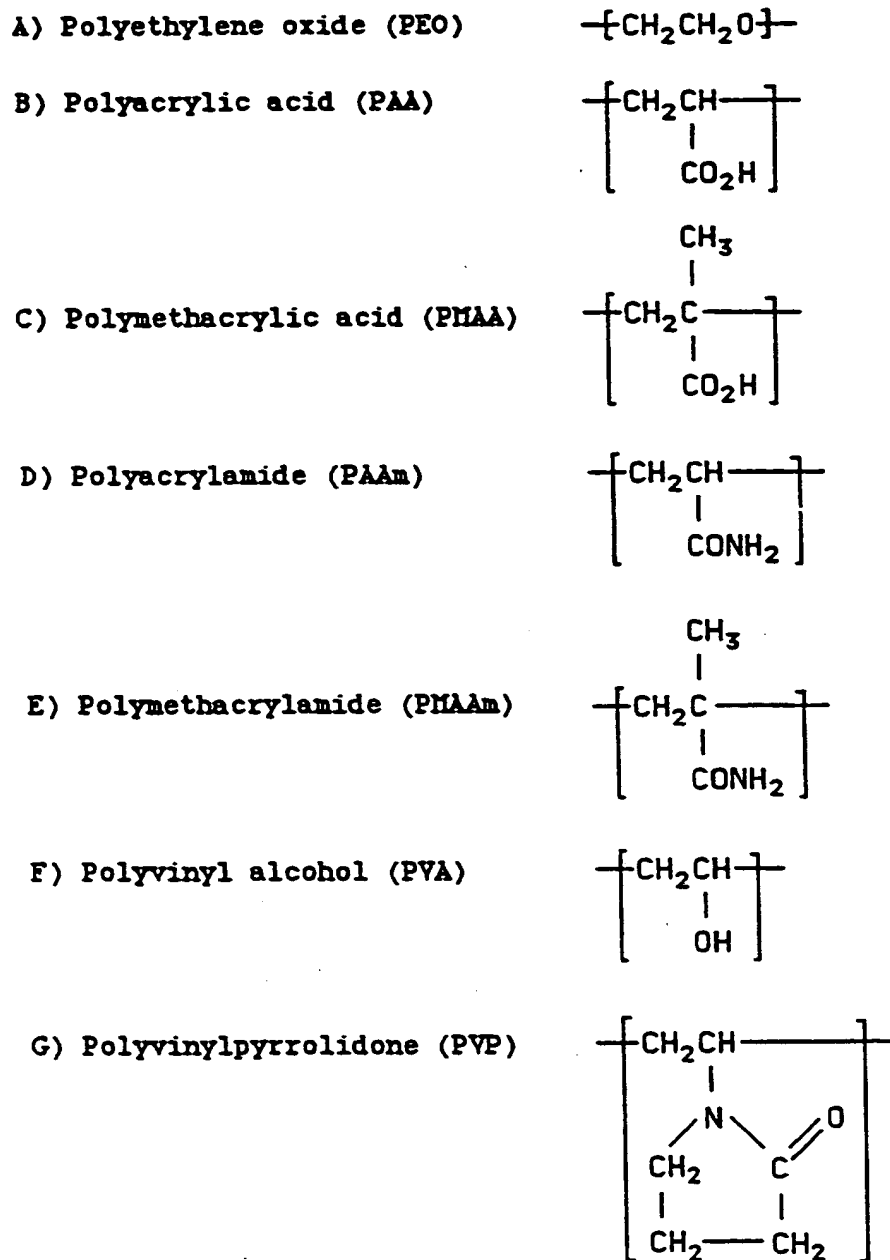


Figure 2.1 Structures of common water-soluble synthetic polymers

Table 2.4
Thermodynamic parameters for polymer-water interactions^a

Water-soluble polymers	χ^b (Temp. (°C), Ref.)	(Unit, Temp. (°C), Mol.wt. $\times 10^{-4}$, Ref.)	$A_2 \times 10^4$	σ (Temp. (°C), Ref.)
PEO	0.45 (27, [62]) 0.44 (23, [63]) 0.41-0.42 (--, [64])	30.8-117.5 (atm·cm ⁶ /g ² , 25, 1.018, [62]) 47.2 (atm·cm ⁶ /g ² , 25, 4.35, [71]) 30.5-36.4 (cm ³ ·mol/g ² , 25, 0.37-0.89, [58])		1.38 \pm 0.06 (20, [62]) 1.95 (--, [60])
PAA	--	--	--	--
PMAA	1.36 (40, [65])	--	--	--
PAAm	0.49 (30, [66]) 0.47 (30, [67])	45.9 (cm ³ /g ² , 25, 39, [62])		2.36 (30, [60]) 2.72 \pm 0.10 (30, [62])
PMAAm	--	0.29 (cm ³ /g ² , 25, 32, [62])	--	--
PVA	0.49-0.50 (--, [72]) 0.49 (30, [68])	3.9-5.2 (cm ³ /g ² , 30, 18-19.6, [62]) 0.82-4.5 (cm ³ ·mol/g ² , --, --, [60])		1.87 (--, [60]) 2.04 \pm 0.1 (30, [62])
PVP	0.58 (25, [69]) 0.49 (30, [70])	3.4 (cm ³ /g ² , 25, 2.45-3.79, [62]) 2.5-64.7 (cm ³ /g ² , 25, 1.95-93.3, [62]) 16.05 (atm·cm ⁶ /g ² , 25, 11.7, [71]) 17.25 (atm·cm ⁶ /g ² , 25, 27.9, [71])		2.55 (--, [60])

^aFor more detailed information, see References involved
^bValues for sufficiently diluted solutions.

$$\Delta S_M = - R(n_1 \ln v_1 + n_2 \ln v_2)$$

and thus,

$$\Delta G_M = RT(n_1 \ln v_1 + n_2 \ln v_2 + RT\chi n_1 v_2)$$

where

ΔH_M is heat of mixing,

ΔS_M is configurational entropy of mixing,

n_1, n_2 are moles of solvent and polymer, respectively,

v_1, v_2 are volume fraction of solvent and polymer,
respectively.

The polymer-solvent interaction parameter χ characterizes the interaction energy per mole of solvent divided by RT for a specific solvent-polymer system. Since v_1 and v_2 are the volume fractions, then the two logarithmic terms on the right-hand side of the above equation are always negative; this allows the value of χ to be positive (up to 0.5, in fact) while still getting complete miscibility (since ΔG_M is then still negative). Considering the effect of molecular weight, for a given mass of polymer and of solvent the term $n_2 \ln v_2$ will become less negative with increasing molecular weight, finally becoming zero in the limit of infinite molecular weight; thus a higher molecular weight for the polymer makes for a less favorable free energy contribution for the mixing process, leading to the well-recognized inverse relation between the solubility of a polymer and its molecular weight. From the equation, $\Delta H_M = RT\chi n_1 v_2$, a positive value of χ corresponds to a positive value of the

contribution ΔH_M , which thus disfavors mixing, while the converse is also true. In the great majority of cases the experimental values of χ are positive. Values of χ up to 0.5 are found for systems showing complete miscibility, while for $\chi > 0.5$ the systems are characterized by only limited miscibility, with higher values of χ corresponding to decreasing extent of interaction of the two components. There are various methods for the determination of χ [57], such as equilibrium swelling, osmotic pressure, vapor pressure, sedimentation, viscosity, optical studies, and inverse gas chromatography.

From the Table, A_2 is the "second virial coefficient" which is a direct characteristic of intermolecular interactions between a solvent and a polymer, or between polymers in a solvent. A_2 can be determined by different methods [57], such as osmometry, ebulliometry (based on the difference between the boiling temperature of a solution and the boiling temperature of the pure solvent), cryoscopy (based on the difference between the freezing temperature of a solution and the freezing temperature of the pure solvent), and light scattering and is then expressed as follows:

i) Osmometry

$$\pi/C = RT/M_n + A_2C + A_3C^2 + \dots$$

$$A_2 = (\rho_s/\rho_p^2 M_s) (1/2 - \chi)$$

ii) Ebulliometry

$$\Delta T_b/C = K_e/M_n + A_2C + A_3C^2 + \dots$$

$$A_2 = (RT^2/\rho_p^2\Delta H_S) (1/2 - \chi)$$

iii) Cryoscopy

$$\Delta T_m/C = K_c/M_n + A_2C + A_3C^2 + \dots$$

$$A_2 = (RT^2/\rho_p^2\Delta H_S) (1/2 - \chi)$$

iv) Light scattering

$$KC/R\theta = 1/M_wP_0 + 2A_2C + \dots$$

$$A_2 = (\rho_S/\rho_p^2M_S) (1/2 - \chi)$$

where

π is osmotic pressure,

C is solution concentration,

R is universal gas constant,

T is temperature,

M_n is number-average molecular weight,

A_2, A_3 are second and third virial coefficients,

respectively,

ρ_S is density of solvent,

ρ_p is density of polymer,

M_S is molecular weight of solvent,

ΔT_b is boiling point elevation,

K_e is ebullioscopic constant

ΔH_S is heat of solvent evaporation (ii) or fusion (iii),

ΔT_m is depression of melting point,

K_c is cryoscopic constant,

K is constant,

R_0 is Rayleigh ratio,

M_w is weight-average molecular weight,

P_0 is scattering factor.

In all cases A_2 is expressed as a function of $(1/2 - \chi)$.

The units of A_2 depend on the way in which it is expressed.

The sign of A_2 is important. A positive second virial

coefficient indicates association between polymer and

solvent molecules or repulsive interactions between polymer

molecules in a solvent such as excluded volume effects or

repulsive electrostatic effects [58]. A negative second

virial coefficient indicates attractive two-polymer

molecular interactions, such as hydrophobic or attractive

electrostatic effects. Negative A_2 is common for highly

charged macromolecules such as proteins, which associate

quite easily. On the other hand, A_2 for nonionic polymers

should always be positive due to excluded volume

considerations (excluded volume is generally defined as the

effective volume of a solution that, strictly for steric

reasons, is not available to molecules or particles as the

result of the introduction of another molecule or particle

[59]). For polymer-solvent interactions, a general rule

(for positive values of A_2) is that

- i) for good solvents, A_2 is high,
- ii) for poor solvents, A_2 is low,
- iii) at $A_2 = 0$, the polymer behaves thermodynamically ideal (i.e., no polymer-solvent interaction).

A_2 is dependent on the temperature and the molecular weight of the polymer.

From the Table, σ is the "steric factor" or "stiffness parameter" characterizing the flexibility of a polymer chain in a solvent [60]. The flexibility of polymer chains depends primarily on the ease of rotation around the bonds on the main chain, which in turn is directly influenced by the nature of the side groups. The steric factor is defined as follows [61,62]:

$$\sigma = (\langle r^2 \rangle_o / \langle r^2 \rangle_{of})^{1/2}$$

where $\langle r^2 \rangle_o$ is an unperturbed mean-square end-to-end distance of a linear chain molecule in solution and can be determined by limiting viscosity number measurements, light scattering, and small-angle X-ray scattering [57]. $\langle r^2 \rangle_{of}$ is a mean-square end-to-end distance of a freely rotating chain. The freely rotating state is a hypothetical state of the chain in which the bond angle restrictions are retained, but the steric hindrance to internal rotation are released. $\langle r^2 \rangle_{of}$ can be readily calculated from the given basic structure of the chain. For instance, if the chain consists of only one kind of bond of length, l , we obtain

$$\langle r^2 \rangle_{of} = nl^2 \{ (1 + \cos\theta) / (1 - \cos\theta) \}$$

where n is a number of bonds and θ is a supplement of the valence bond angle (for more discussion, see Ref.61). Since in a real polymer chain some hindrance to free rotation is invariably present, the steric factor is always greater than 1, the more so, the lower the ease of rotation about the bonds on the main chain, i.e., the lower the chain flexibility.

As seen in Table 2.4, PEO shows lowest values of χ among the water-soluble synthetic polymers, which means complete miscibility of PEO with water ($\chi < 0.5$). The anomalous behavior of PEO in water is explained as a result of strong interaction via hydrogen bonds of water molecules with the ether oxygens of the polymer chains [49-51]. In the case of the A_2 , it is hard to compare directly the values in the Table because the units of A_2 are different depending on the experimental methods used. However, as we compare the values of PEO and those of PVA or PVP with same units, PEO shows much higher values of A_2 than PVA or PVP, which means that PEO is highly interactive with water (water is a better solvent for PEO than for PVA or PVP) and PEO chains are highly repulsive towards each other in water. Flory [56] suggested, by his "dilute solution" treatment, that A_2 can be regarded as expressing the volumes mutually excluded by neighboring polymer molecules (i.e., excluded volumes). Thus, PEO in water will have a larger excluded volume than

PVA and PVP or other water-soluble polymers. σ values of PEO are also lower than other water-soluble polymers as seen in Table 2.4, which is considered as verification of a flexibility of PEO chains. Higher σ values for PAAM or PVP may be due to bigger side bulky groups which restrict the chain flexibility.

Molecular motions on a time scale in the range between pico- (10^{-12}) and micro- (10^{-6}) seconds can be investigated by nuclear magnetic relaxation. The dynamic behavior of polymers in aqueous solution generally shows motional components in this range, which is characterized by "correlation times" (or "reorientation times"). Nuclear magnetic relaxation is driven by the modulations of local nuclear interactions, e.g., ^1H - ^{13}C dipolar coupling and C-D quadrupolar coupling. The chain segment mobility, responsible for the modulation of the coupling, depends on the flexibility of the polymer chain. The correlation time (τ_c) is regarded as the average time that the molecule requires to rotate through an angle of one radian [73,74]. In the solid state, where motion is hindered, τ_c is large. The local dynamics of polymers in aqueous solutions depend on concentration and molecular weight of polymers. The concentration dependence is caused by polymer-polymer interactions, whereas in the concentration independent range the polymer dynamics is mainly determined intramolecularly and by solvent-polymer interactions. Molecular weight

dependence is caused by end group contributions [35]. Molecular weight dependence of the relaxation is not observed, in the case of PEO, when the chain length is greater than about 100 [35,42].

In the pure liquid at room temperature the water molecules tumble about with a mean τ_c of about $2.5-10 \times 10^{-12}$ sec (2.5-10 ps) [75,76]. We wanted to compare τ_c values for water-soluble polymers; however, we could obtain only a few comparison results because the data available for polymers in aqueous solution were scarce and different conditions were used. Breen et al. [35] determined τ_c for PEO in D₂O solution at a temperature of 25 °C. They applied dilute solution of PEO to avoid polymer-polymer interactions. They found that τ_c values for PEO are in the ranges of 15-100 ps depending on the conditions used and those values are a factor 30 smaller than found for PMAA [36], illustrating the high flexibility of the PEO chain. Lang et al. [38] compared τ_c values of PEO in dilute solutions, determined by nuclear magnetic relaxation measurement and electron spin resonance. They obtained similar values of τ_c for PEO in various solvents to those of Breen et al. [35] and suggested that both methods indicate the highly flexible nature of this polymer.

2.7 Conclusions

It appears that PEO in water has rapid motions [35-45,77-79] and a large excluded volume [58,80-82] compared to the less water-soluble or insoluble polyethers and other water-soluble synthetic polymers.

As we consider the structures of the polyethers (Table 2.3) and water-soluble synthetic polymers (Figure 2.1), we can expect that PEO will be most flexible in water among those polymers because it does not have bulky groups attached to the backbone and is uncharged. Thus, PEO segments will not be sterically hindered in water and will be highly mobile (Table 2.4).

PEO molecules are highly interactive with water, as evidenced by the high values of second virial coefficient (or low values of polymer-solvent interaction parameter). However, PEO molecules will minimally perturb the structure of water itself because they will nicely fill out water lattice points (by oxygen atoms) and voids in the water structure (by ethylene segments) without distortion of water lattices if the suggestion by Kjellander and Florin [28,29] is true; Other polyethers or water-soluble polymers will distort water structure due to the unsuitable distances of neighboring and next-neighboring ether oxygen atoms or bulky side groups.

The unique solution properties of PEO in water, such as almost unlimited solubility, good structural fit between PEO and water, high mobility, large excluded volume, and

hydrophilicity, are closely related to the protein resistance of PEO surfaces (discussed in Chapter 3).

2.8 References

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